COATINGS

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BARRIER COATINGS FOR TYPE C/SiC CERAMIC-MATRIX COMPOSITES (REVIEW)

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The change in the compositions of thermal barrier and antioxidant coatings for C/SiC composite materials was examined. Data are reported on the compositions and properties of bi-, tri-, and multilayer coatings. The mechanism of the barrier effect of several compositions is elucidated. The prospects for use of the new compositions of barrier coatings for increasing the temperature of use of the composite materials are demonstrated.

Aviation and space engineering, transport systems, the chemical industry, and thermal and atomic energetics cannot evolve without creating new construction materials suitable for working in extreme conditions — in exposure to high temperatures and pressures, ionizing radiation, dynamic loads, different aggressive media, high gas and liquid flow rates, etc. Such materials are usually created at the same time that methods for protecting them from negative factors are developed.

Intensive research has been conducted in the past ten years on developing composite materials based on nonoxide compounds — carbon, silicon carbide and nitride, etc., in which these compounds can be both matrix and reinforcing filler in the form of continuous or separate fibers, whiskers, and plates (C/C, C/SiC, SiC/SiC composites). These materials are distinguished by high strength characteristics, heat resistance, and low weight, which allows using them in aviation and space engineering as high-temperature construction materials, for fabrication of gas turbine, diesel engine, and heat-exchanger parts, and in triboengineering [1, 2].

In reducing conditions, C/SiC composite materials retain high mechanical property indexes up to a temperature of 2000°C, but in oxidizing conditions, their use is limited by the possibility of oxidation of the carbon at temperatures above 400°C. The SiC/SiC composites were more resistant to high-temperature oxidation due to formation of a barrier layer of SiO_2 on the surface of the composite material. How-

ever, in the presence of water vapors, oxidation and volatilization of gaseous products of the reaction are intensified according to the reaction:

$$SiO_2 + 2H_2O = Si(OH)_4.$$
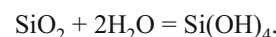
For this reason, the use of SiC/SiC composites in humid air is limited by temperatures of 1200 – 1300°C [3, 4].

One possible method for solving this problem is to develop functional barrier ceramic coatings. As a function of the composition of the composite materials, the conditions of their use, and correspondingly the requirements imposed, the coatings can fulfill different functions:

improve the mechanical properties of the support in a temperature gradient;

limit chemical processes of oxidation and corrosion of the composites;

regulate heat transfer at high temperatures of use of the article by changing the thermal conductivity of the material [5].

The analytical review by BCC Research reports the results of marketing studies in the North American market for high-efficient ceramic coating technologies in 2004 – 2009. It was noted that the total production volume of this kind had $1.1 billion in 2004, and the share of high-strength items was 14%, cutting and processing tools was 17%, and approximately 64% of the market was for coatings for engine components. In 2009, the market volume is projected to increase to $1.6 billion, with annual average growth of 7.6%, while coatings for engine components will constitute 68%. The re-

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sults of estimating the production volume dynamics obtained by different methods, in particular, thermal spraying, physical and chemical deposition from the gas phase (PVD and CVD), etc. (dipping, sol-gel, microoxidation, using laser technologies). As the data in Fig. 1 show, thermal spraying is the basic method of obtaining ceramic coatings. The annual increase in the volume of these articles is 8.5%, primarily due to the fast development of aviation and space engineering. For goods manufactured by PVD and CVD methods, lower five-year growth rates are projected: 5.8 and 5.0%, respectively.

The compositions of the functional coatings must satisfy certain requirements; the fundamental ones are a high melting point, resistance to oxidizing atmospheres and water vapors, low thermal conductivity, and the main one, CLTE values close to the CLTE of silicon carbide. Materials with dominant crystalline phases containing silicates and aluminosilicates — mullite, cordierite, strontium and barium aluminosilicates, and rare-earth element silicates — satisfy these requirements to the greatest degree [2, 6 – 8].

Mullite, $3Al_2O_3 \cdot 2SiO_2$, is of the greatest interest as a barrier coating for silicon carbide (nitride) due to the low CLTE and high chemical stability. Beginning in the 1980s, coatings made from mullite and/or binary systems of Al_2O_3 and high-melting oxides (ZrO_2, Y_2O_3, etc.) were used for thermal barrier composite materials (thermal barrier coatings — TBC). These coatings significantly increased the crack resistance of the articles [9, 10].

Later, in the 90s, second-generation compositions were developed for barrier coatings for composites — bilayer chemically stable barrier coatings (environmental barrier coating — EBC). A number of conditions must be taken into account in selecting compounds that can fulfill the function of a barrier layer:

The compounds must be thermodynamically stable and chemically stable in the entire temperature range in the conditions of use of the articles;

the barrier layer must have compatible physicomechanical properties with the support and the coating;

the barrier layer must decrease the rate of chemical and diffusion processes in the transition layer between support and coating.

A barrier coating was developed (US Patent Nos. 5869146 and 6129954) for silicon-containing ceramics consisting of layers of mullite and zirconium oxide stabilized with 8%[2] Y_2O_3 (YSZ). Mullite has a CLTE intermediate between the CLTE of SiC and YSZ, so that the binder layer of mullite ensured good adhesion with the support. However, the comparatively high activity of the silicon oxide in the mullite caused rapid decomposition of the coating by water vapor. The YSZ composition as the top coating layer provided protection at high temperatures in conditions of high humidity. This composition was selected for the top coating, since it had already been successfully used at the time for thermal barrier coat-
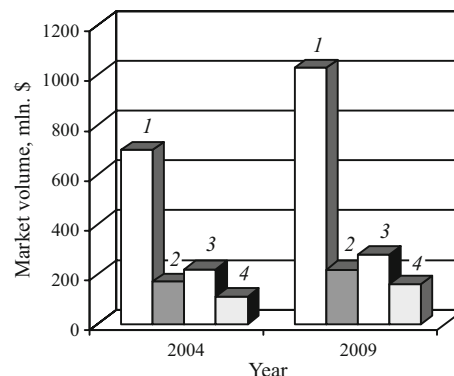
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[2] Here and below: mass content.

Fig. 1. North American market volume of highly efficient ceramic technologies in 2004 – 2009 (based on BCC Research data). Manufacturing methods: *1*) thermal spraying; *2*) physical vapor deposition; *3*) chemical vapor deposition; *4*) other methods: dipping, sol-gel, microoxidation, laser technologies.

ings on metals and alloys in gas turbine engines. The bilayer coatings protected the ceramics from water vapors at a temperature of approximately 1300°C during hundreds of hours of use, but on long exposure, the water vapors penetrated the barrier layer through cracks, acting on the silicon-containing support, which led to peeling of the coating [10] US Patent No. 5985470 proposed using compositions based on barium and strontium aluminosilicates (BSAS) of the general type $(1 - x)BaO \cdot xSrO \cdot Al_2O_3 \cdot 2SiO_2$ $(0 \leq x \leq 1)$ as the binder layer, and zirconium oxide totally or partially stabilized with yttrium oxide and silicates as the coating layer.

The third generation of barrier coatings was developed jointly as a result of research programs at Glenn Research Center (NASA), General Electric Co., and Pratt and Whitney in the US (US Patent No. 6410148) [11]. This type of coating consists of three layers, each with its own functional application. The lower (ground) layer of silicon ensures good adhesion with the support; the middle layer is mullite or mullite + BSAS composite; the top layer is BSAS, which has thermal barrier properties due to the low thermal conductivity. All of the layers are applied by a modified plasma spraying method. This type of coating was introduced by Solar Turbine Co. (USA) for the internal lining of the combustion chambers in gas-turbine engines.

The results of prolonged industrial tests of SiC/SiC composite construction elements in 1997 – 2004 showed an increase in the lifetime at a temperature of 1250°C to 14 – 17,000 h. In addition, the increase in the working temperatures decreased the volumes of nitrogen oxide and CO emissions by 2 and 5 times — to < 15 and < 10 ppm, respectively [12].

Another type of compositions was proposed in US Patent No. 6296942. Silicon-containing ceramics (C/SiC, SiC/SiC, SiC/Si_3N_4) or metal alloys (Mo, Nb, Fe, Fe – Ni) with silicon can be used as supports. The binder (ground) layer between the substrate and middle layers can be SiO_2 or metal silicides on which the middle layer, containing mullite,
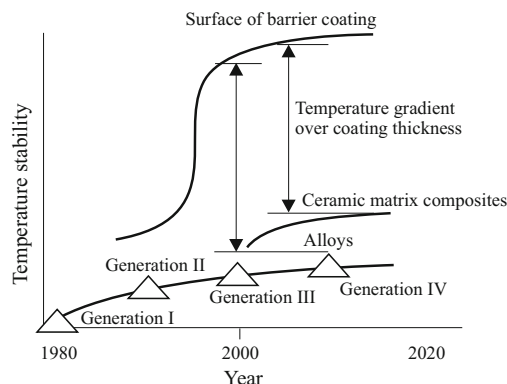
Fig. 2. Change in the temperature stability of composite materials and alloys with thermal barrier coatings.
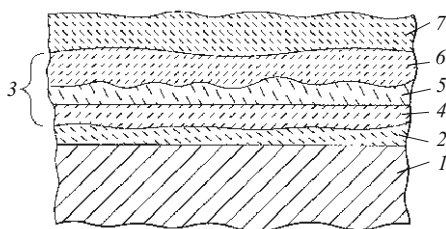

Fig. 3. Structure of multilayer antioxidant thermal barrier coating for silicon-containing nonmetallic supports: *1*) nonmetallic support, ceramic or ceramic-matrix composite made of silicon carbide (nitride); *2*) inner layer of Al_2O_3 or SiO_2, optimum layer thickness of 5 – 1, optimum layer thickness of 5 – 15 μm; *3*) middle layer consisting of three sublayers: *4*) mullite, *5*) alkaline-earth element aluminosilicates (predominantly BSAS; due to the low thermal conductivity, this layer provides good protection from external high temperatures), *6*) mullite, aluminum oxide and/or alkaline-earth element aluminosilicates and YSZ, whose concentration gradually increases to the top layer, *7*) hafnium and zirconium oxides; the optimum thickness of this thermal barrier layer is 125 – 750 μm.

BSAS, mullite + yttrium silicate, mullite + calcium silicate is applied. The mullite content is 40 – 80% and the content of the other silicates is 20 – 60%. The top, barrier layer contains calcium aluminosilicate of the composition (%): 24 CaO, 40 Al_2O_3, 36 SiO_2. Each layer is 70 – 150 μm thick.

The dynamics of the change in the temperature stability of composite materials and alloys with different thermal barrier coatings is shown in Fig. 2. The important increase in the temperatures of use (up to 1500°C) significantly increases the effectiveness of many structures. In gas turbines, the increase in the maximum temperature increases the efficiency, decreases fuel consumption, and also reduces harmful emissions. In aircraft structures, increasing the acceptable temperatures of construction elements allows reducing their weight and increasing the useful load weight and flying speed and distance.

Research is currently continuing on developing new barrier coating compositions which would further increase the

working temperatures on the surface of the coating to more than 1500°C and the temperature gradient over the coating thickness by no less than 170°C while preserving the lifetime of the articles over hundreds of hours [11].

A new type of antioxidant coating for C/C – SiC composites fabricated by liquid-phase infiltration of silicon is described in [13, 14]. The surface layer of cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) used as the barrier coating was applied by vacuum plasma spraying, while the inner layer of BoraSiC® was applied by the CVD method. The multilayer BoraSiC® coating is in turn a trilayer structure in which layers of silicon carbide are separated by a layer of B_4C ($SiC – B_4C – SiC$). This layer is approximately 200 μm thick. Self-healing of the cracks that appear in the coating is due to oxidation of SiC to SiO_2 and B_4C to B_2O_3 that takes place at temperatures above 1100 and below 950°C, respectively. Formation of a glass phase and stopping access of oxygen to the carbon fibers through microcracks are the consequence of this reaction. The oxidation resistance was determined at 1000 – 1500°C for 100 – 1000 h. The results of tests at 1500°C showed that growth of cracks arising in the middle layer stopped at the cordierite – BoraSiC® interface so that both the strength and the oxidation resistance of the composite increased markedly. Use of the cordierite layer allowed prolonging the lifetime of construction elements by 7 times. One cause of this positive effect is the low CLTE of cordierite: $(10 – 20) \times 10^{-7} K^{-1}$.

The compositions of thermal barrier coatings can differ. US Patent No. 7348287 reported fabrication of a ceramic material which can be used for heat- and/or corrosion-resistant coatings for ceramic-matrix composites. The ceramic contains 40 – 60% yttrium silicate and 40 – 60% ZrO_2 stabilized with Y_2O_3. This ceramic material has a porous structure (20 – 40% porosity) and provides good heat insulation for the surface of the composite due to the low thermal conductivity: 1 – 3 W/(m · K). A combination of alkaline-earth and rare-earth element aluminates is proposed as the middle layer in US Patent No. 7357994: $YAlO_3$, $Y_3Al_5O_{12}$, $NbAlO_4$, $SrAl_2O_4$, $CaAl_2O_4$, $CaAl_4O_7$, $MgAl_2O_4$, $ScAlO_3$, etc.

Multilayer coatings with up to 6 – 8 layers are now used for thermal protection of composites. The structure of the coating developed in US Patent No. 6607852 to protect silicon-containing composites is shown in Fig. 3. The technology for manufacturing such multilayer coatings includes heat treatment after application of all of the layers, required for formation of the crystalline phase of BSAS, ensuring interconnection between the layers, and removing stresses in the structure of the coating.

US Patent No. 6759151 proposes a multilayer coating with a low CLTE. The outer coating consists of rare-earth element silicates ($R_2O_3 \cdot SiO_2$, $2R_2O_3 \cdot 3SiO_2$, $R_2O_3 \cdot 2SiO_2$, where R is Sc, Dy, Ho, Er, Tm, Yb, Lu, Eu, Gd, Th, or a combination of them). Mullite, magnesium, calcium, and barium aluminosilicates, and anticorrosion compositions — hafnium oxide and silicate, scandium and ytterbium silicates

— are used as the middle layers. The outer layer consists of rare-earth element silicates and hafnium and zirconium oxides and silicates. The CLTE of the layers varies within the limits of $(40 - 60) \times 10^{-7}$ K^{-1}, which ensures strong adhesion with the support. Such coatings are stable at 1400°C for 300 h with a thermocycling load with a cycle length of 1 h in an atmosphere simulating combustion conditions: 90% $H_2O - O_2$. Use of high-melting hafnium and zirconium oxides (melting points of 2758 and 2715°C) ensures a further increase in the working temperatures of the articles to 1650°C. In addition, the coatings are stable in air and humidity.

The properties of solids are determined not only by their chemical composition, but also by the features of the crystal structure caused by the method of fabrication. For this reason, intensive research is being conducted both on developing coating compositions with new chemical properties and creating methods of applying them on composite materials. At present, different methods are used for fabricating coatings on composite materials: application from suspensions, immersion, chemical vapor deposition (CVD), air and vacuum plasma spraying (APS and VPS, respectively). Methods of applying the coatings from solutions, sol-gel technology, for example, are used for fabricating some oxide coatings. This is a promising method of obtaining high-temperature materials that allows reducing the synthesis temperature and regulating the structure and properties of the materials by varying the conditions of synthesis. This provides for greater fine granularity of the coating and the possibility of applying thin layers of coating on articles of complex shape.

In selecting coating compositions for composite materials, it is first necessary to consider the values of the CLTE of the compounds, since they determine the character of the stresses that arise due to temperature drops and correspondingly the strength, temperature stability, and in the final analysis, the character of failure [15 – 17].

CLTE of Some Compounds Most Frequently Used As Constituents of Composite Barrier Components

Material	CLTE, 10^{-7} K^{-1}
Si	35 – 45
Mullite	64
Celsian:	
monoclinic	40 – 45
hexagonal	80
YSZ	About 100
Y_2SO_5	30 – 50
SiC	59

Minimal stresses due to the closeness of the CLTE arise on the boundary of the silicon carbide and mullite layers. The effect of the nature of the stresses in coatings on the temperature stability of the articles was investigated in [18 – 20]. BSAS compound (celsian) forms two polymorphic modifications — monoclinic and hexagonal — which differ significantly, by almost two times, in the value of the CLTE. The
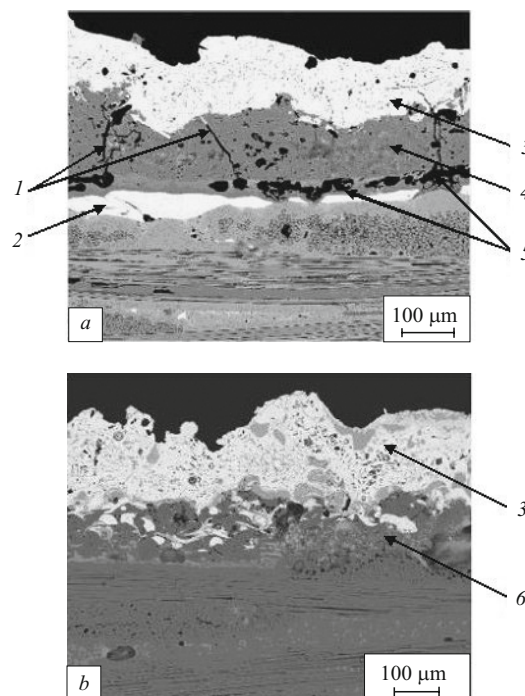

Fig. 4. Microstructure of a protective barrier coating after high-temperature heat treatment. Composition of coating: *a*) Si/mullite/BSAS; *b*) Si/mullite + BSAS/BSAS; *1*) cracks; *2*) silicon; *3*) BSAS; *4*) mullite; *5*) pores; *6*) mullite + BSAS.

temperature of the polymorphic transition is 1590°C. Based on a study of BSAS phase equilibrium in coatings obtained by plasma spraying, it was shown in [11, 15] that both modifications are present in the compositions, and the concentration of the hexagonal form is a function of the conditions of deposition of the coatings and can be varied with respect to the layer thickness.

In addition to the thermomechanical properties, great attention is being focused on studying the reaction boundary of the support – coating interface; the processes that take place on the boundary of the layers at high temperatures and in an oxidizing atmosphere; the diffusion kinetics and the mechanism of the corrosive action. The microstructure of a protective barrier coating based on a SiC/SiC composite is shown in Fig. 4 after heat treatment at 1300°C for 1000 h in an atmosphere of 90% $H_2O - O_2$. Cracks appear in the middle mullite layer, which causes diffusion of oxygen and formation of bubbles on the boundary of the mullite and silicon layers. Incorporation of up to 20% BSAS in the middle layer sharply reduces the probability of cracking. In the opinion of the researchers in [15], this is due to the better deformation properties of the composite, since Young's modulus is 150 GPa for mullite and 100 GPa for BSAS.

The change in the mass of the article (% or mg/cm^2) as a result of surface reactions is a quantitative characteristic of the temperature stability of materials. At high temperatures, the weight of the samples can both increase due to oxidation of SiC in conditions of a humid atmosphere, and the weight
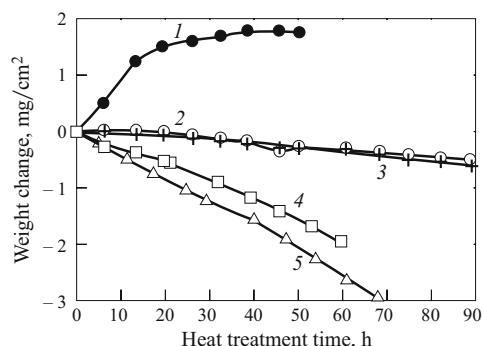
Fig. 5. Kinetics of the weight change of SiC and SiC/SiC compositions with different coatings at 1300°C and pressure of 600 kPa. Composition of coating: *1*) Si/mullite + BSAS/YSZ; *2*) Si/mullite/BSAS; *3*) Si/mullite + BSAS/BSAS; *4*) SiC/SiC composite fabricated by the infiltration method; *5*) SiC fabricated by CVD.

of the support can also decrease due to evaporation of the SiO_2 formed. According to the data in [15], a weight change greater than $1 - 3\%$ can be considered critical and unacceptable. The dependences of the kinetics of the weight change of the initial composites obtained by the infiltration and CVD methods and supports with coatings of different composition are shown in Fig. 5. The use of a barrier coating based on a combination of layers of mullite and BSAS can significantly reduce weight losses in the samples after treatment at 1300°C for 100 h. Using YSZ as the cover layer causes marked weight gain after $10 - 20$ h due to oxidation of the support. The results obtained indicate a good correlation between the magnitude of the stresses in the barrier coating, the probability of it cracking, and in the final analysis, the stability of silicon carbide ceramics with coatings.

The aerospace industry is one of the basic purchasers and users of composite materials. Composites are widely used in manufacturing heat-loaded parts of promising aircraft engine

units (rocket nozzles, turbine blades, engine flaps, and other structural elements). In modern aircraft, the highest temperatures (up to $1650 - 1800$°C) are created in regions of strong heating — in the pump part of the fuselage and the front part of the wings. For this reason, it is necessary to develop new compositions for thermal barrier coatings with a temperature of use of 2000°C and higher for creating the new supersonic aircraft that return space ships of the Buran and Shuttle type.

Some physicochemical properties of the compounds used in thermal barrier and antioxidant coatings are reported in Table 1.

For ceramic-matrix composites, silicon-containing coatings are effective for a relatively long time at temperatures below 1650°C due to formation of a layer of SiO_2 which has an inhibiting and healing effect. Coatings based on hafnium compounds withstand higher temperatures of use but tend to crack, work poorly in conditions of thermocycling loads, and retain some porosity up to $1800 - 2000$°C, which provides only partial protection for the composites.

A more promising way of creating a new generation of thermal barrier and antioxidant coatings consists of developing compositions based on oxygen-free compounds — borides and carbides. Information has recently appeared on creation of technology for production of multilayer coatings of HfC/SiC composition by Ultramet Co. (USA). Such coatings were used to protect composites based on a zirconium diboride matrix with reinforcing carbon fibers. The test results showed that samples of the materials withstood relatively prolonged, for 140 min, temperatures of approximately 2300°C. Due to the low thermal conductivity, the temperature gradient on the surface of the coating and the layer of the carbon-containing support reached 480°C. Brief heating of the coating protected the composite for 60 sec at 2837°C.

These data reflect the current advances in synthesis of thermal barrier coatings and make it possible to determine the most promising directions for further improving composites using a new generation of barrier coatings.

TABLE 1

Compound	Melting point, °C	CLTE, 10^{-7} K^{-1}	Density, g/cm^3	Thermal conductivity, W/(m · K)
Si_3N_4	1900	–	3.44	–
B_4C	2347	56	2.52	30
SiC	2700	53	3.31	120
ZrO_2	2715	75	5.60	$1 - 2^*$
HfO_2	2758	68	9.68	–
ZrB_2	3246	–	6.12	–
HfB_2	3250	–	10.50	–
ZrC	3540	73	$6.59 - 6.73$	20
C	3550 3827*	100	2.25	150
HfC	3890	68	12.70	22

* US Patent No. 7348287.

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